

Characterization of Organic Functional Groups in  
Model Systems for Coaly Matter Employing  $^{19}\text{F}$  NMR

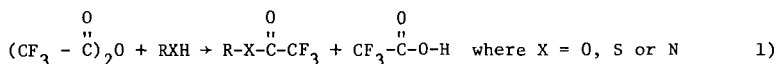
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INTRODUCTION

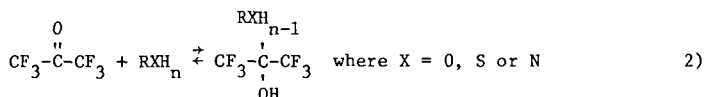
The characterization of complex organic mixtures has been explored using  $^{19}\text{F}$  NMR to introduce a fluorine "tag" into molecules containing hetero atom functional groups. The  $^{19}\text{F}$  NMR approach was suggested because it is nearly as sensitive as  $^1\text{H}$  NMR and has a much wider range of chemical shifts (~375 ppm vs. ~15 ppm for  $^1\text{H}$ ). This range indicates that fluorine chemical shifts are more sensitive to subtle changes in molecular structure when compared to  $^1\text{H}$ . An added advantage of  $^{19}\text{F}$  NMR is that most analytical samples of interest (e.g., coal products) contain no fluorine alleviating the inherent background problem when compared with  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques.

The use of  $^{19}\text{F}$  nmr to characterize organic functional groups was first suggested by Manatt (1), who used trifluoroacetic anhydride as the reagent for the introduction of a "fluorine tag" into the molecules of interest. Manatt examined various trifluoroacetic acid esters formed from various alcohols which have characteristic  $^{19}\text{F}$  nmr chemical shifts dependent upon whether the substrate was a primary, secondary or tertiary alcohol. The general reaction for this reagent is indicated below.



Later, other studies extended the trifluoroacetic anhydride approach to other organic functional groups including phenols (2), steroids (3), and hydroxy groups in poly(propylene oxides) (4).

Another  $^{19}\text{F}$  reagent, hexafluoroacetone, was suggested by Leader (5) for the characterization of various functional groups. The adduct (formation of hexafluoroacetone with active hydrogen compounds) is indicated below.



This reagent has been utilized for characterization of alcohols, amines, mercaptans and other active hydrogen containing compounds (5-9). Preparation of the adducts is easily accomplished *in situ* by bubbling the reagent gas (hexafluoroacetone) into a solution of the sample and solvent. Although the equilibrium indicated in equation 2 strongly favors the adduct product on the right for most primary alcohols and many other simple systems, the equilibrium tends to shift to the left for more complex and/or sterically hindered active hydrogen containing functional groups (10). Obviously, this feature limits the scope of this reagent if quantitative data is desired.

By comparison, it should be mentioned that  $^1\text{H}$  nmr reagents (i.e. hexamethyl-disilazane (11), acetic anhydride (12), dichloroacetic anhydride (13), etc.) have also been developed for characterizing functional groups. Unfortunately, most of

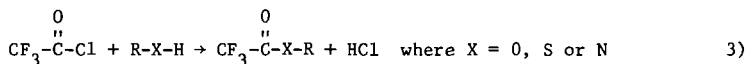
these reagents typically yield  $^1\text{H}$  nmr spectra with relatively small chemical shift ranges (0.1 - 0.4 ppm). That is, for even partial characterization of the various possible functional groups encountered in coal product samples (e.g., phenols, carboxylic acids, alcohols, etc.), the highest available nmr field strengths (super-conducting magnets) are normally employed (14) with the  $^1\text{H}$  nmr reagents presently available. In contrast, the range of  $^{19}\text{F}$  chemical shifts for numerous model systems observed for the hexafluoroacetone adducts and trifluoroacetyl derivatives are -10 ppm and -1-2 ppm, respectively. These results reinforce the basic premise that  $^{19}\text{F}$  nmr chemical shifts are usually more sensitive than  $^1\text{H}$  shifts to subtle changes in molecular structure.

## RESULTS AND DISCUSSION

In the present study, preliminary nmr examination of the reaction products of the trifluoroacetic anhydride ( $^{19}\text{F}$  nmr), hexafluoroacetone ( $^{19}\text{F}$  nmr), and hexamethyldisilazane ( $^1\text{H}$  and  $^{13}\text{C}$  nmr) reagents discussed in the Introduction with typical model compounds and actual solvent refined coal fractions indicate a number of limitations with these reagents. This point is particularly true in utilizing these reagents for relatively complex coal product samples. Based on these initial findings, it was deemed appropriate to establish certain criteria necessary for an "ideal" nmr reagent for general characterization of a wide range of different functional groups. These criteria are listed below.

- 1) The ideal nmr reagent should not require harsh preparation conditions and only very limited manipulations should be involved in the preparation procedure.
- 2) The nmr reagent should react quantitatively and side reactions should be kept to a minimum.
- 3) The scope of the nmr reagent would be enhanced if derivative preparation could be accomplished in various solvents.
- 4) The nmr "probe nuclei" for the reagent should be very sensitive to subtle changes in molecular structure.
- 5) Ideally, a complimentary feature of item 4 would be the availability of selective nmr reagents. That is, reagents which would only detect the presence of certain specific functional groups.

With these criteria in mind, new  $^{19}\text{F}$  nmr reagents have been examined. The first of these is trifluoroacetyl chloride which yields the same derivatives as the trifluoroacetic anhydride reagent (1-4) (Equation 3).



This reagent is a gas (b.p.  $-18^\circ\text{C}$ ) and derivatives are easily prepared in situ by bubbling the reagent into a solution consisting of the sample and solvent at temperatures from  $-50^\circ\text{C}$  to  $-10^\circ\text{C}$ . Various solvents have been utilized including chloroform or chloroform-d, tetrahydrofuran, and methylene chloride. The entire preparation procedure can be carried out in the sample nmr tube. This represents a distinct advantage in the derivative preparation when compared with the trifluoroacetic anhydride reagent. In addition, the by-product of this reaction is HCl compared with  $\text{CF}_3\text{CO}_2\text{H}$ , the by-product formed with the trifluoroacetic anhydride reagent, which in many cases causes a large interfering peak in the  $^{19}\text{F}$  spectra of these derivatives. It should be noted, however, that if water is present in the sample, the trifluoroacetic acid peak also appears in the  $^{19}\text{F}$  nmr spectrum when trifluoroacetyl chloride is the reagent.

The initial phase of the trifluoroacetyl chloride study was an examination of suitable trifluoroacetyl derivative preparation procedures, the range of  $^{19}\text{F}$  chemical shifts for model systems, and typical yield data for this reagent. A typical  $^{19}\text{F}$  spectrum for the trifluoroacetyl derivative obtained from benzyl alcohol is indicated in Figure 1. The reference at 0.0 ppm in these spectra is 1,2-difluorotetrachloroethane ( $\text{CFCl}_2\text{CFCl}_2$ ) and was the  $^{19}\text{F}$  reference employed in most of this work. The trifluoroacetyl chloride reagent reacts with primary, secondary, tertiary alcohols, benzyl alcohols, amines, phenols and thiols. The by-product of the reaction,  $\text{HCl}$ , does not interfere in the  $^{19}\text{F}$  NMR spectrum.

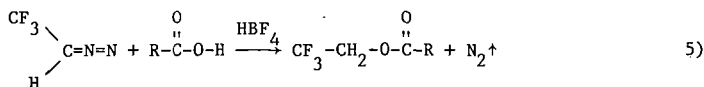
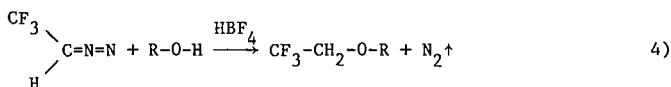
Certain reactions, particularly those of phenols and amines were quite slow. A study was conducted to see if using a nucleophilic base would improve the reactions. Those bases which were tried were pyridine, triethyl amine, 2,6-lutidine, and 4-dimethylaminopyridine (DMAP). Based on reaction yields, 2,6-lutidine and DMAP appear to be the best catalysts. It has been shown previously that DMAP is an excellent acylation catalyst (17).

A side reaction which can occur using this reagent is the formation of trifluoroacetic acid. This interference, however, can easily be removed by allowing the reaction mixture to stand over a small amount of  $\text{K}_2\text{CO}_3$ . The acid peak is entirely removed from the spectrum. The peak which occurs from excess trifluoroacetyl chloride is also readily removed by degassing the sample with  $\text{N}_2$ .

It appears that the derivatives formed using trifluoroacetyl chloride are well-resolved in the  $^{19}\text{F}$  NMR spectra as indicated by figure 2 with only a couple of regions of overlap. The overall chemical shift range is about 2 ppm. It appears that this reagent will be useful as an analytical tool for characterization of functional groups. All interferences in the spectrum can be removed and the reactions occur in high yield with the proper choice of catalyst.

A second and entirely new class of  $^{19}\text{F}$  nmr reagents under examination is fluorinated diazoalkanes. Diazomethane with and without a Lewis acid catalyst has been extensively used in organic chemistry for preparation of methyl ester and methyl ether derivatives (15). An obvious extension of this approach would be the use of a fluorine containing diazo reagent.

The first fluorinated diazoalkane examined in this study was trifluorodiazomethane (16). We have found that this reagent reacts smoothly with alcohols, phenols and carboxylic acids at room temperature to  $-10^\circ\text{C}$  in the presence of a catalyst (typically  $\text{HBF}_4$ ) to yield fluorinated ethers and esters according to equations 4 and 5.



One of the disadvantages of this reagent using our present reaction conditions is the water present in the added catalyst (50% water solution of  $\text{HBF}_4$ ). The trifluorodiazomethane reacts with the water to yield 1,1,1-trifluoroethanol and bis (1,1,1-trifluoroethyl) ether.

The  $^{19}\text{F}$  spectra for these derivatives appear as triplets ( $^{19}\text{F}$ - $^1\text{H}$  coupling to methylene protons). However, singlet spectra can be obtained by  $^1\text{H}$  decoupling.

Figures 2 and 3 indicate the range of  $^{19}\text{F}$  chemical shifts observed for a number of model compounds using the trifluoroacetyl chloride and trifluorodiazethane reagent, respectively. In general, the yields are somewhat higher for the trifluorodiazethane reagent. The chemical shift range, however, appears to be slightly larger for the trifluoroacetyl derivatives. Nevertheless, both of these reagents have potential advantages over other reagents previously employed.

Figure 4 is the first spectrum obtained from the acid fraction of an Amax solvent refined coal (SRC) sample using the trifluoroacetyl chloride reagent. The large peak at  $\sim 8.5$  ppm is trifluoroacetic acid. The peak centered at  $\sim 7.6$  ppm with fine structure is undoubtedly due to phenols and perhaps benzyl alcohols. The peaks between 7.7 ppm and 8.4 ppm indicate limited presence of aliphatic alcohols. The broad peak centered at  $\sim 7.4$  ppm has not been assigned at the present time. Although these are only the first results obtained from the  $^{19}\text{F}$  nmr reagents, the number of resolved lines in several SRC fractions indicate that the  $^{19}\text{F}$  nmr approach is indeed a promising technique. Results applying the  $^{19}\text{F}$  nmr approach to additional coal products will be discussed in this presentation.

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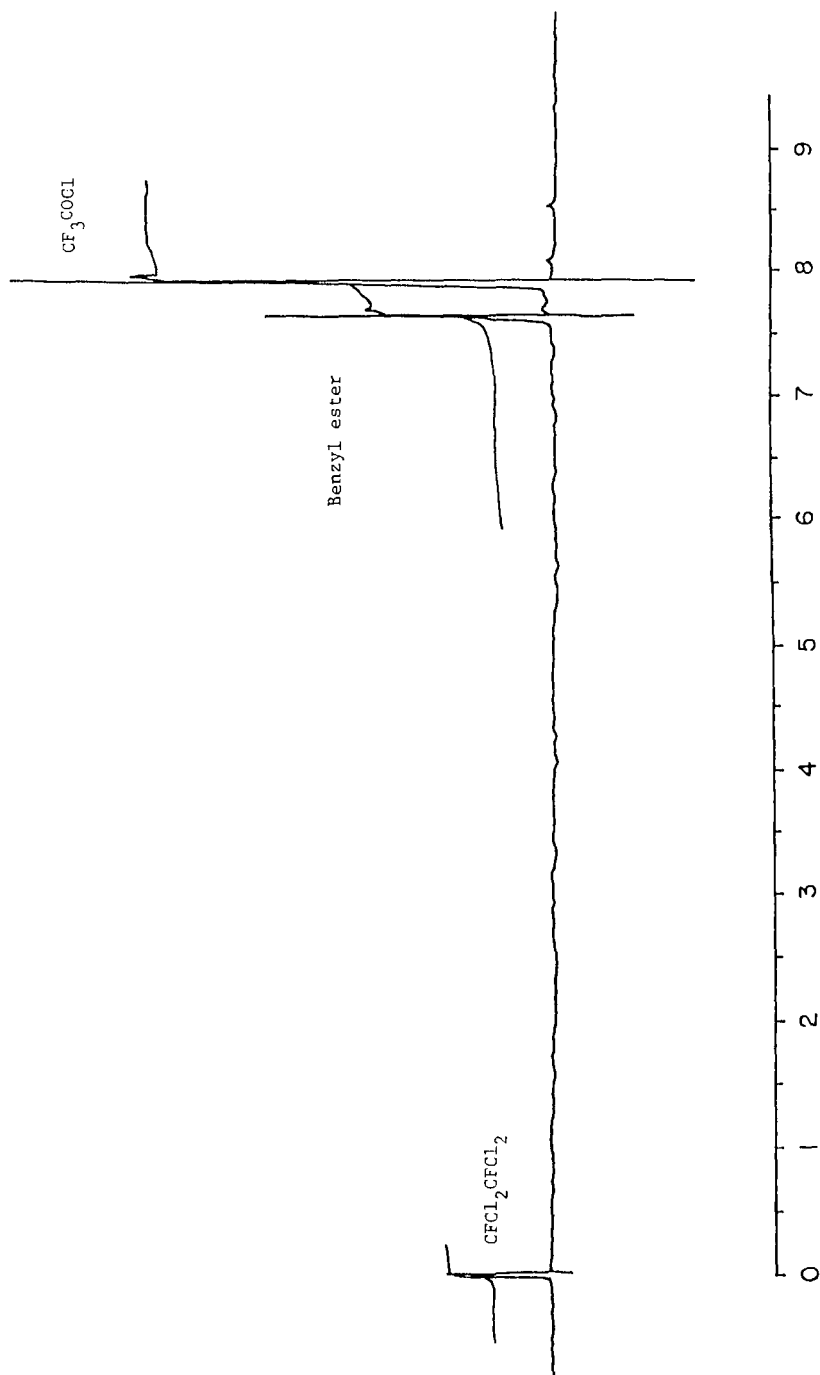


Fig. 1.  $^{19}\text{F}$  nmr spectrum of solution prepared by reacting benzyl alcohol with trifluoroacetyl chloride, solvent is chloroform-d with 1,2-difluorotetrachloroethane used as the reference.

$^{19}\text{F}$  CHEMICAL SHIFTS OF DERIVATIVES  
USING  $\text{CF}_3\text{-C(=O)-Cl}$

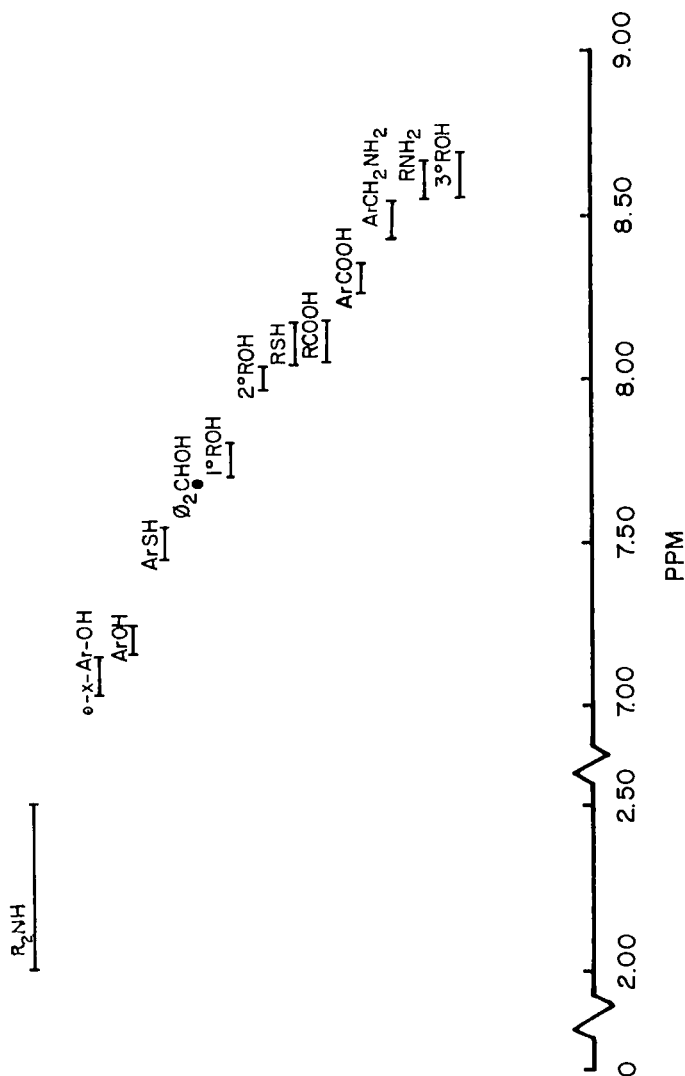


Fig. 2. Range of  $^{19}\text{F}$  nmr chemical shifts observed for trifluoroacetyl derivatives of model compounds with 1,2-difluoroethane used as the reference.

<sup>19</sup>F CHEMICAL SHIFTS OF  
TRIFLUOROETHYL ESTERS AND ETHERS

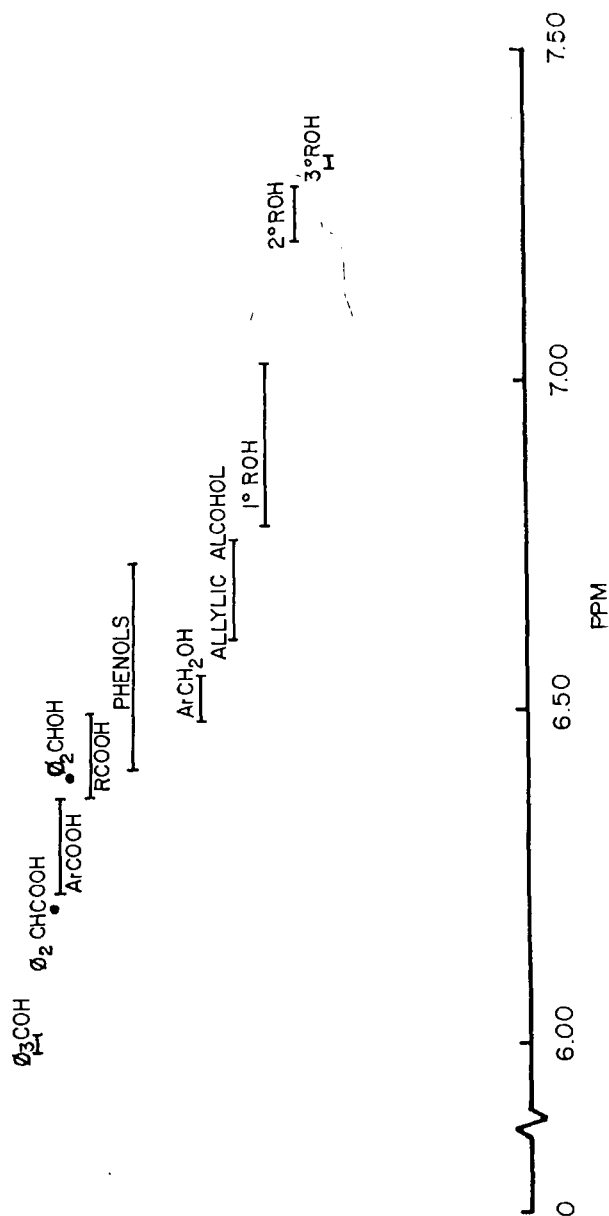


Fig. 3. Range of <sup>19</sup>F nmr chemical shifts observed for trifluorodiazooethane derivatives of model compounds with 1,2-difluoroethane used as the reference.



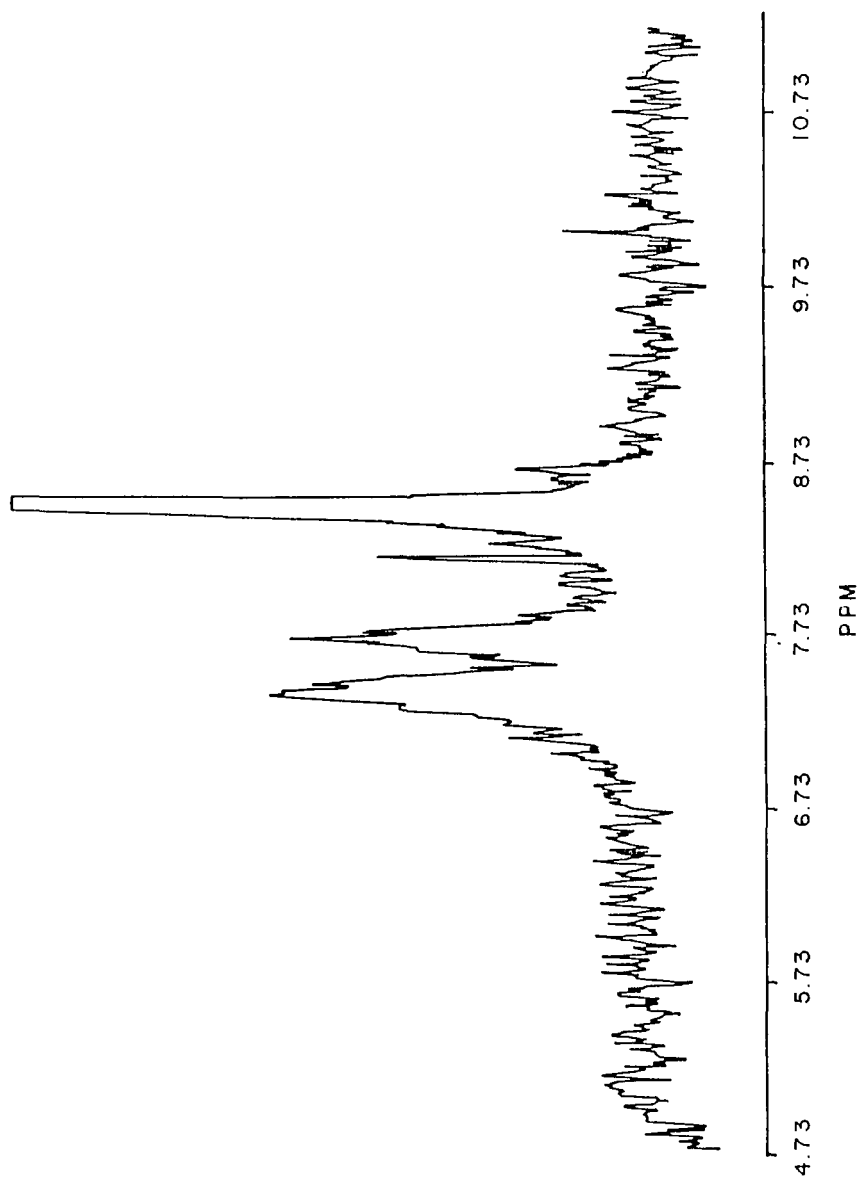


Fig. 4.  $^{19}\text{F}$  FT nmr spectrum of reaction mixture of trifluoroacetyl chloride and Amax SRC acids fraction, solvent is chloroform-d with 1,2-difluoroethane used as the reference.